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(21) International Application Number: PCT/US97/18296 (22) International Filing Date: 13 October 1997 (13.10.97) (30) Priority Data: 08/732,021 16 October 1996 (16.10.96) US (71) Applicant: ENVIRONMENTAL TEST SYSTEMS, INC. [US/US]; 23575 County Road 106, Elkhart, IN 46514 (US). (72) Inventors: EVTODIENKO, Yuriy Vladimirovich; Puschino "B" -28-50, Moscow Region, 142292 (RU). MEDVEDEV, Boris Ivanovich; Apartment 26, Puschino, V-29, Moscow Region, 142292 (RU). (74) Agent: STEPHENSON, Harry, T.; 23575 County Road 106, Elkhart, IN 46514 (US).		(81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DEVICE AND METHOD FOR THE DETERMINATION OF WATER (57) Abstract A test device and method are described for directly determining the liquid phase water content of organic solvents and indirectly the liquid phase water content of solids. The device and method utilize a reagent composition consisting basically of the dried residue of a mixture of 1. a colorimetric indicator material, preferably a cobaltous or cuprous salt and 2. a polymeric water vapor barrier material, such mixture incorporated into a matrix which is contacted with or immersed into the liquid test sample, removed therefrom and the color change of the test composition correlated with a standard color chart to give a quantitative result of the amount of water in the test sample. When the method is applied to solids, the water must first be extracted from the solid using a substantially anhydrous extracting fluid such as reagent alcohol.		

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DEVICE AND METHOD FOR THE
DETERMINATION OF WATER

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Field of the Invention

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The present invention relates to a dry reagent test device and method for directly determining the water content of liquids and indirectly the water content of solids. The dry reagent test device is typically a flat matrix material containing the dried residue of a colorimetric test composition which responds quantitatively to the water content of fluids. The method comprises contacting the device with water either dissolved in a water miscible solvent or water suspended in a liquid system or in the case of determining water in solids, first extracting the water with an anhydrous solvent and thereafter contacting the extractant with the test device.

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Background of the Invention

The determination of water in various liquids and solids is almost universally included in a complete chemical analysis, the rationale for and importance of such determination being peculiar to the material being tested. In some instances water content can adversely affect the material while in others it can enhance the performance or value of the material. For example, in the automotive fluid area, the water content of the ethylene glycol cooling fluid can dramatically enhance the freezing point of the mixture while water in the ABS brake fluid can adversely affect the performance of the auto braking system.

Moreover, the water content of solid materials such as chemicals and food stuffs can positively or negatively affect the taste, performance and/or stability thereof. Accordingly, there is a need for an easy to use, safe, and reasonably accurate chemical method and test device for determining the water content of a large variety of materials. The present test meets such needs directly for determining the water content of liquids and indirectly for determining the water content of solids which can be extracted with water miscible solvents.

As noted above, the water content of fluids used in anti-locking brake systems (ABS) is of particular interest. Such fluids commonly use glycol derivatives, such as triethylene glycol monomethyl ether, as the liquid base. It has been found that over a period of time such fluids absorb moisture which in turn lowers the boiling point of the fluid. When this happens, especially during warm weather and when brakes are continuously used such as in a long downhill descent, the fluid could boil, resulting in a complete loss of the braking system. Consequently, it is becoming necessary

to routinely test such fluids for water content and discard the material when it reaches a predetermined level of water contamination.

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Description of the Prior Art

Generally, water analysis is either done by testing for water in the vapor phase (humidity) or for water in the liquid phase as a component of either another liquid or a solid material. Testing for humidity is probably the most common type of water determination and is usually accomplished using an instrument known as a hygrometer or a simple chemical test device using an inorganic metal salt impregnated into a paper matrix which responds to water vapor to give a colored response. The metal salt devices date back to the 1940's and have been the subject matter of numerous patent and literature references. Exemplary of the patent references are U.S. Patent Nos. 2,460,065 to 2,260,074. More specifically, U.S. Patent No. 4,034,609 which discloses and claims a more sophisticated device which gives a digital indicia of humidity using such salts also recites some of the many patent references as well as literature references in column 3, lines 48 to 64.

The second type of testing, commonly used in the analytical chemistry laboratory, is for the determination of the liquid water content of various solid or liquid materials using a chemical test reagent system and possibly an instrumental readout system for measuring the response of the reagent system. Exemplary of the sample materials that are commonly tested for water content are grains, organic chemicals, solvents, oils, biological materials and so forth. This type of chemical water testing can also be further broken down into the actual technique used to determine the water content of the material being tested. The present invention deals with

a colorimetric chemical method for determining the liquid water content of a sample and the prior art recited herein will be limited to such chemical methods.

Instruments will not be addressed in this discussion of the prior art.

Chemical methods for determining liquid phase water date back to the early part of the twentieth century; however, by far the most popular and accurate chemical method for the determination of water is based on the so-called Karl Fischer reagent. This method was first introduced in 1935 and is the subject matter of several books including the classic text by Mitchell and Smith titled "Aquametry", Interscience Publishers, Inc., New York, 1948. This textbook gives an excellent background and history of water determinations including the technical details of the Karl Fischer methodology as well as other chemical methodologies, including the use of inorganic metal salts for determining the vapor phase water content of hydrocarbon gases (Chapter 1, page 8).

More recently, U.S. Patent No. 5,224,373 to Williams et al. discloses and claims a multilayer humidity in air sensor which comprises a first water vapor barrier material on one side of a layer sensitive to water vapor and a third layer of water vapor permeable plastic material. In use the sealed system is exposed to humid air which permeates the water vapor permeable layer to reach the humidity sensing layer to give a color response to the degree of exposure to water vapor.

Finally, U.S. Patent No. 5,520,041 to Haswell discloses a medical sample system which utilizes the Williams et al. cobaltous chloride humidity sensing device and further refers to U.S. Patent 2,214,354 to Snelling which discloses a composition which absorbs moisture which in turn activates a dyestuff to give an visual indication of the moisture present in the atmosphere.

Summary of the Invention

The present invention relates to an easy to use,
5 disposable, dip and read test device for determining the
amount of water present in various liquid and solid
materials. When used to determine the liquid phase water
content of solids, the test sample must first be
extracted with a water miscible anhydrous solvent such as
10 absolute alcohol and then the solution of water in
solvent contacted with the test device. The test device
itself consists essentially of a liquid sample absorbent
matrix containing the dried solids of a water sensitive
reagent system which, in use, is contacted with the
15 sample to be tested, removed therefrom and the developed
color compared to a color chart, other indicia of water
concentration or algorithm to give a quantitative value
of the amount of water present in the sample. The
reagent system comprises 1. a chemical indicator material
20 which is responsive to water to give a color change
proportional to the amount of water present in the sample
and 2. a polymeric water vapor barrier material which
functions to protect the indicator material during
processing and use.

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Description of the Preferred Embodiments

Dip and read test devices, commonly known as reagent
strips, have been in extensive use, especially in the
30 medical area, for the past thirty to forty years. Some
simpler test strips, such as litmus paper, go back even
much further in time. Such devices commonly utilize an
absorbent matrix consisting of either paper or other flat
synthetic liquid absorbent fibrous materials or membranes
35 into or onto which a colorimetric reagent system can be
incorporated and subsequently dried. The resulting

structure can be either attached to a plastic handle or used by itself to contact the fluid being tested, withdrawn and the resulting color change read and interpreted.

5 The exact mechanism of how the present device works is not known with certainty but in its simplest form, the reagent system of the present invention comprises two essential components. The first is a water sensitive indicator material which responds to the presence thereof
10 by either changing color in proportion to the amount of water present or by simply increasing in color intensity. The term "change in color" therefore is intended to encompass either an actual change from one color to another, such as in changing from blue to pink or simply
15 changing from a light shade of blue to a more intense shade of the same blue color. Either way, the change in color must be proportional to the amount of water present in the sample being tested.

 The indicator materials of the present invention are
20 basically metal salts which give a color response to the presence of water. Preferred indicator materials are the cobaltous and the cuprous halides and thiocyanates such as cobaltous bromide (Br_2Co), cobaltous chloride (Cl_2Co), cobaltous iodide (I_2Co), cuprous bromide (Br_2Cu), cuprous
25 chloride (Cl_2Cu), cuprous iodide (I_2Cu), and cobaltous thiocyanate [$\text{Co}(\text{CNS})_2$]. Other metal salts which respond in a similar manner may also be used in the present invention. An amount of indicator to give a visual response to the concentration of water present is usually
30 used, the preferred amount to respond to about five percent water in the liquid phase sample solution is from about 40 mg/ml to about 100 mg/ml of metal halide as used in the impregnating solution. Obviously, the amount of actual indicator in the matrix depends upon the size,
35 absorbency and volume of the matrix. Combinations of metal salts to give the best color changes in response to

water or to eliminate or obviate color interference in or by the sample solution may certainly be advantageously utilized.

The second essential component of the present reagent composition is a water vapor barrier material. The purpose of this component is to allow the water in the sample solution to react with the indicator material when the device is contacted with or immersed in the sample fluid but prevent the water vapor in the air or environment from reacting with the indicator once the test device has been removed from the sample solution and the color development allowed to go to completion and be read in the open air. This is especially important when the device is used as a field test and is exposed to very high humidity levels.

The vapor barrier materials are polymeric substances which are soluble in a substantially anhydrous solvent and have limited solubility in water. The polyethylene and polypropylene glycols having molecular weights of from about 400 to about 35,000 have been found to be particularly useful as water vapor barrier materials with the preferable molecular weight being from about 400 to about 2000. Other barrier materials which have been found to be useful in the present invention are poly (vinyl chloride) (PVC) and poly (vinyl pyrrolidone) (PVP). Combinations of various vapor barrier materials may also be advantageously used in formulating the composition of the present invention.

The matrix which incorporates the test composition of the present invention is basically a flat, relatively thin, sheet or roll of material which has absorbent or bibulous properties. Advantageously, this matrix can be made from natural or synthetic fibrous substances such as filter paper, polyester, glass fibers, membranes, and so forth. Usual methods may be used to incorporate or impregnate the test composition into the matrix; however,

since this is a test device for determining water, precautions must be in place to ensure that all of the raw materials are dry and that the environment in which the processing takes place has a relative humidity of
5 less than about 25% percent.

After incorporating the reagent system into the matrix, it is preferable to attach an appropriate sized area of the matrix to a strip of water and solvent impervious plastic material, which strip serves as a
10 handle to facilitate immersing the matrix and reagent into the sample being tested. Such handle also serves to isolate the actual test reagent from being contaminated or ruined by contacting the reagent area with moisture from the fingers of the analyst.

15 The method of using the device to test for water in a liquid test sample is fairly straightforward. The test device is simply immersed into the fluid being tested, removed and after a predetermined length of time, usually less than a minute, the color of the test area is
20 compared to a color chart which has been prepared using a standard set of water concentrations in an acceptable anhydrous solvent. An alternative method of use would be to use a reflectance device to measure the color developed on the strip and interpret such color in terms
25 of water concentration in the sample being tested.

As previously noted, when solid materials such as food stuffs are being tested for water content, the sample must first be pulverized and the water extracted therefrom using an anhydrous water miscible solvent.
30 After filtering, if necessary, the sample is tested in the usual manner. Obviously, precautions must be take to protect the sample and test area from environmental moisture contamination.

Actual processing conditions and testing parameters
35 are exemplified by but should not be limited to the Examples which follow.

Examples

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Example 1

A first reagent composition was prepared by dissolving 500 mg of cobaltous iodide (CoI_2) and 0.2 ml polypropylene glycol (m.w.425) in 5 ml of reagent ethyl alcohol. A length of Whatman F322-02 paper was dipped into this mixture and dried at 110°C for ten minutes. Upon dipping into the mixture the paper was teal blue in color and upon drying became light lime green after drying. The dried paper was cut into 0.2 by 0.2 in. squares and using double faced adhesive tape such squares attached to the end of a strip of reasonably rigid sheet of plastic material 3.25 in. by 0.2 in. All processing of such strips was done in a room having a relative humidity of less than 10%. The strips were stored in tightly capped bottles with desiccant.

A second composition was prepared as detailed next above except that the polypropylene glycol was omitted. Reagent strips were made as described above and also stored in bottles with desiccant. In preparing this second batch of strips, it was noted that within seconds the paper started to turn pink and upon drying the strips became a dark gray color. Upon removal from the drying oven, the strips became a light lime green color but developed pink and red splotches.

The strips containing the polymer were then dipped into brake fluid samples (DOT 3 and 4) known to have a water content of 0, 1, 2, 3, 4, and 5%. Such strips changed from gray green to light olive green depending on the amount of water in the brake fluid. The strips which did not have the polymer changed to a yellowish green and

could not be used against a series of standard color blocks. When both sets of reacted strips were exposed to atmosphere moisture of approximately 25% relative humidity, the strips containing the polymer were
5 unchanged for six hours while the strips which did not contain the polymer changed color significantly within three hours.

Example 2

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The above example was repeated except that polyethylene glycol (m.w. 35,000) was substituted for the polypropylene glycol. When processing and when dipped into varying concentrations of water in brake fluid, the
15 strips reacted in a similar way to those in Example 1.

Example 3

Varying concentrations of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were
20 dissolved in reagent ethyl alcohol to give 1%, 3% and 5% water content. The samples were tested with the strips containing the vapor phase barrier of Example 1. The color change from gray green to light green indicated the water content of the solution contributed by the hydrated
25 aluminum nitrate.

What is claimed is:

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1. A test device for determining the liquid phase water content of an organic solvent comprising an absorbent matrix containing the dried residue of a reagent composition consisting essentially of the

10 following:

A. A colorimetric indicator material quantitatively responsive to the presence of water selected from the group consisting of cobalt and copper salts; and,

15 B. An effective amount of a polymeric water vapor barrier material capable of preventing the reaction of the indicator material with atmospheric moisture upon contact therewith.

2. A test device as in claim 1 wherein the
20 indicator material is selected from the group consisting of cobaltous and cuprous halides and thiocyanates and combinations thereof.

3. A test device as in claim 1 wherein the
25 polymeric material is selected from the group consisting of polyethylene glycol and polypropylene glycol.

4. A test device as in claim 2 wherein the
indicator material is selected from the group consisting
30 of cobaltous chloride and cobaltous iodide.

5. A test device as in claim 4 wherein the indicator material is cobaltous iodide.

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6. A colorimetric method for quantitatively determining the liquid phase water content of an organic solvent, such method capable of being used in the open atmosphere containing an amount of moisture therein, the method comprising:

A. Contacting the solvent for a predetermined time with a dip and read test device consisting essentially of a fluid absorbent matrix containing the dried residue of a test composition containing a colorimetric indicator quantitatively responsive to the presence of water in the solvent and an effective amount of a polymeric water vapor barrier material capable of preventing the reaction of the indicator material with atmospheric moisture;

B. Removing the test device from contact with the solvent and allowing the color response of the indicator material to develop in the open atmosphere;

C. Measuring the degree of color response of the indicator; and,

D. Using a correlating means, determining the amount of water in the solvent from the degree of color response of the indicator.

7. A method as in claim 6 wherein the colorimetric indicator is selected from the group consisting of cobaltous and cuprous halides and thiocyanates and combinations thereof.

8. A method as in claim 6 wherein the polymeric water vapor barrier material is selected from the group consisting of polyethylene glycol and polypropylene glycol.

9. A method as in claim 8 wherein the colorimetric indicator is selected from the group consisting of cobaltous iodide, cobaltous chloride and combinations thereof.

10. A method as in claim 9 wherein the colorimetric indicator is cobaltous iodide.

5 11. A method as in claim 6 wherein the organic solvent sample results from extracting a solid, water containing material therewith.

10 12. A method as in claim 11 wherein the organic solvent is an anhydrous alcohol.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/18296

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G01N 31/22, 33/18
US CL : 73/61.43

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 73/61.43, 61.44, 53.01; 422/68.1, 69, 56, 57, 58, 82.65; 436/ 41, 42, 39, 169, 170

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPTO APS

Search Terms: water, cobaltous iodide, humidity, dissolve, polymer, polyethelene glycol

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, 3,389,967 A (HRABINSKI) 25 June 1968 (25/06/68), see col. 10 lines 59-72.	1-12
Y	US 2,761,312 A (LINE et al) 04 September 1956 (04/09/56), see col. 2 lines 59-70.	1-12
Y	US 5,290,516 A (GRECO et al) 01 March 1994 (01/03/94), see col. 3 lines 53-57.	4, 5, 9, and 10
Y	WO 86/00711 A (OLSSON) 30 January 1986 (30/01/86), see page 4 lines 1 +	11, 12
A	US 3,901,657 A (LIGHTFOOT) 26 August 1975 (26/08/75), see entire document.	1-12
A	US 4,061,468 A (LANGE et al) 06 December 1977 (06/12/77), see entire document.	1-12

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,232,710 A (RIECKMANN et al) 01 February 1966 (01/02/66), see entire document.	1-12